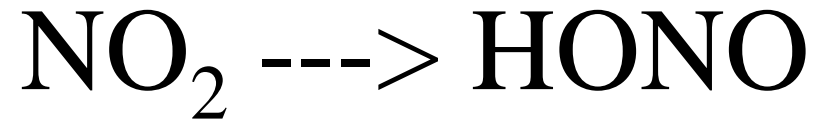# NOx Chemistry in the Polluted PBL

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some possible reactions on soot

- $2NO_2 + H_2O \rightarrow HNO_3 + HONO$ R1
- $NO_2 \rightarrow HONO$ R2
- $HNO_3 \rightarrow NO_2$ R3
- $HNO_3 \rightarrow NO$ R4

NO$_2$ ---> HONO

- NO$_2$ to HONO conversion rates highest at 3.7E-03(Ammann et al., 1998, Nature, 395),with reaction probablity of 0.01
- HONO photlysis rates are of the order of 1.0E-03 (factor of 3 slower than the heterogenous reaction).
- This would imply a large reservoir of HONO even during the day time.

- The lower end of the NO_2 to HONO reaction probablity is reported to be 3.3E-04. This leads to conversion rates of 9.0E-05 mol/cm3-sec of NO_2.
- This would allow for night time build up
- What about $2NO_2 = HONO + HNO_3$?.
- This leads to large buildup of HNO_3 , essentially converting all of NO_2 to either HONO or HNO_3.

- Since HNO_3 reconversion rates through gas phase reactions are quite slow, one would have to invoke a 'soot' reaction to reconvert HNO_3 to NO_2.
- The reported rates of conversion of HNO_3 to NO_2 on 'carbon soot' are of the order of ($\gamma=0.021$). Giving rates of the order of those observed for NO_2 to $HONO + HNO_3$ (Larry et al., 1997, JGR).
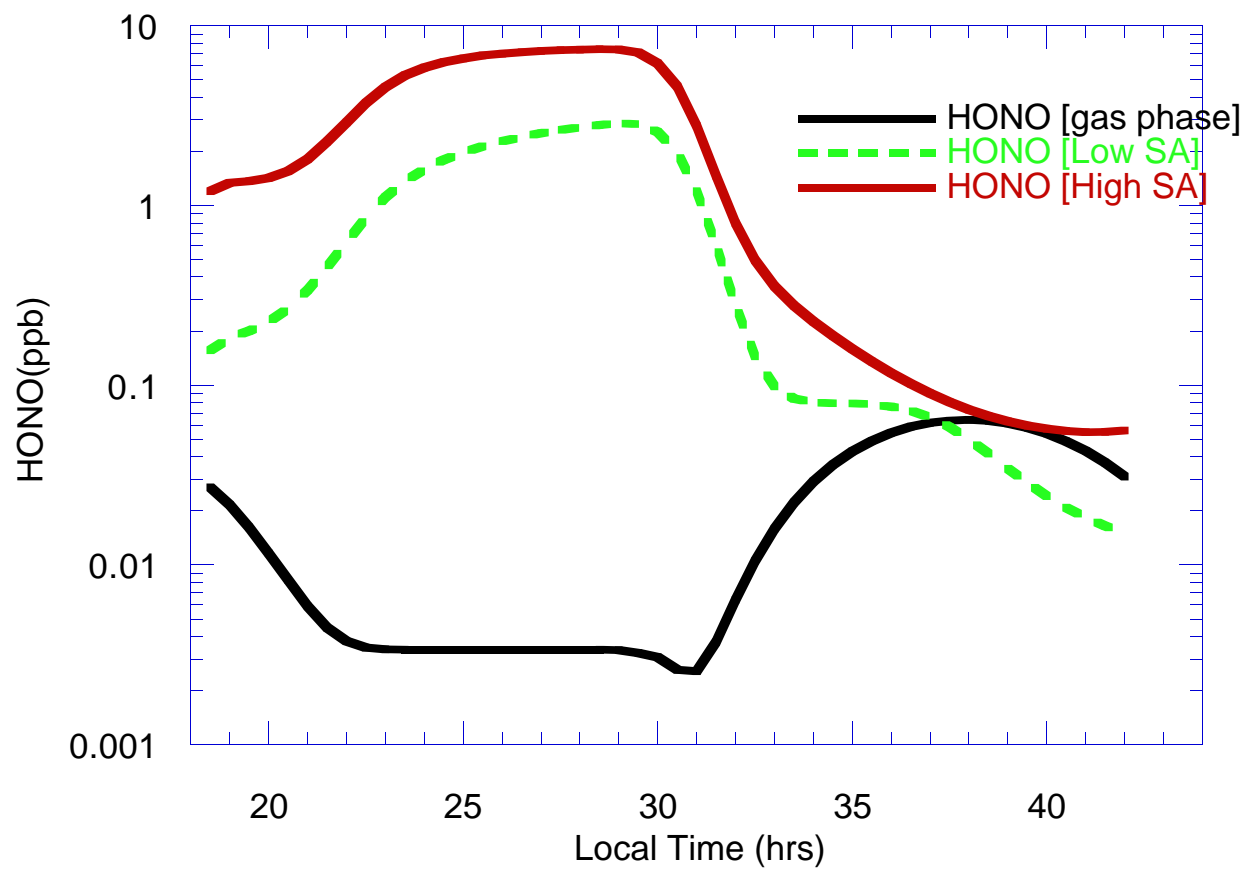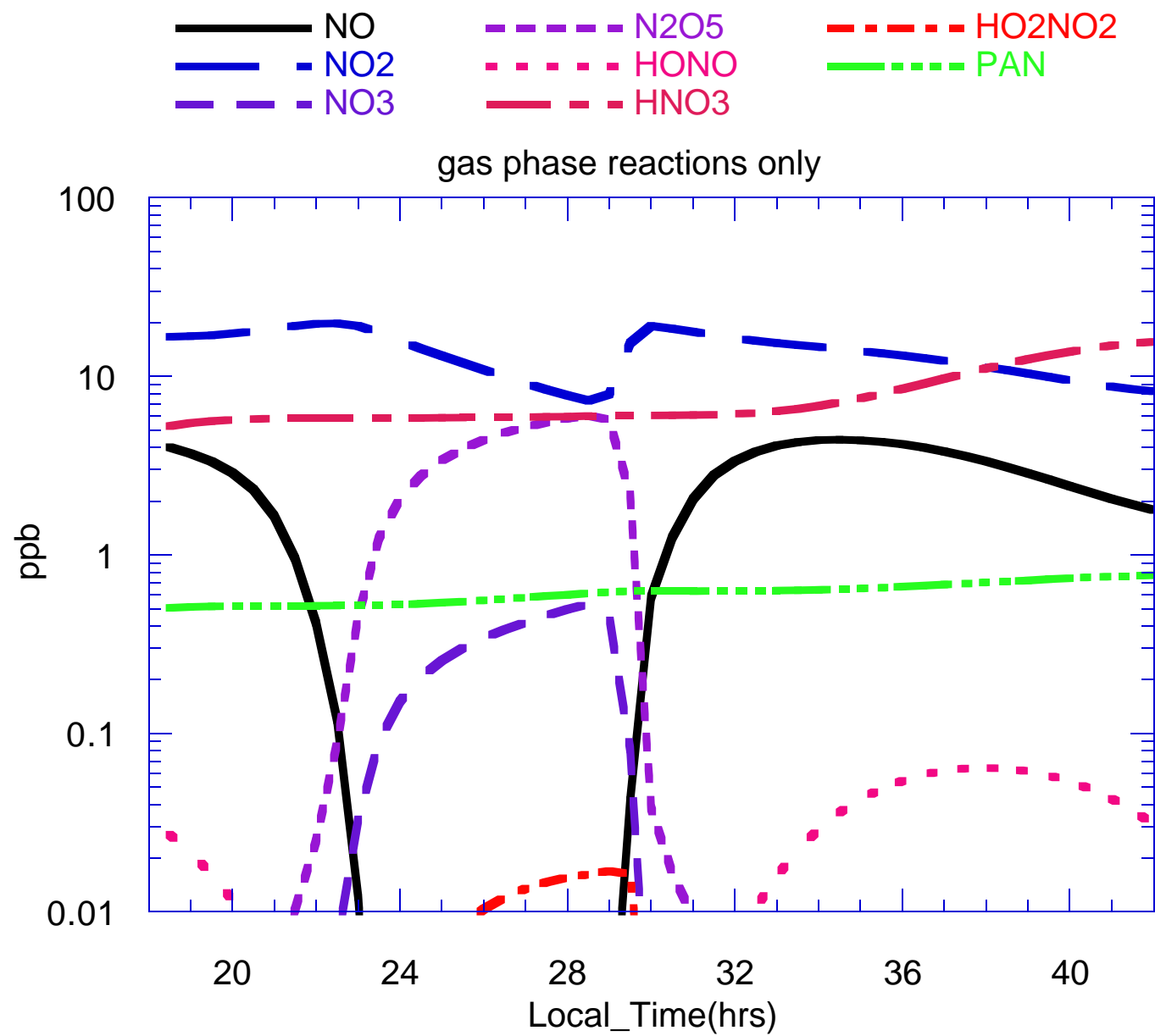
Box-Model

- 72 species
- 152 thermal and 55 photolytic reactions
- Two-stream multiple layer radiative transfer model
- chemical evolution equations solved using Gear method.

- several heterogeneous reactions included.
- one day calculation, starting at 0.0 hours GMT and ending 24 hours GMT.
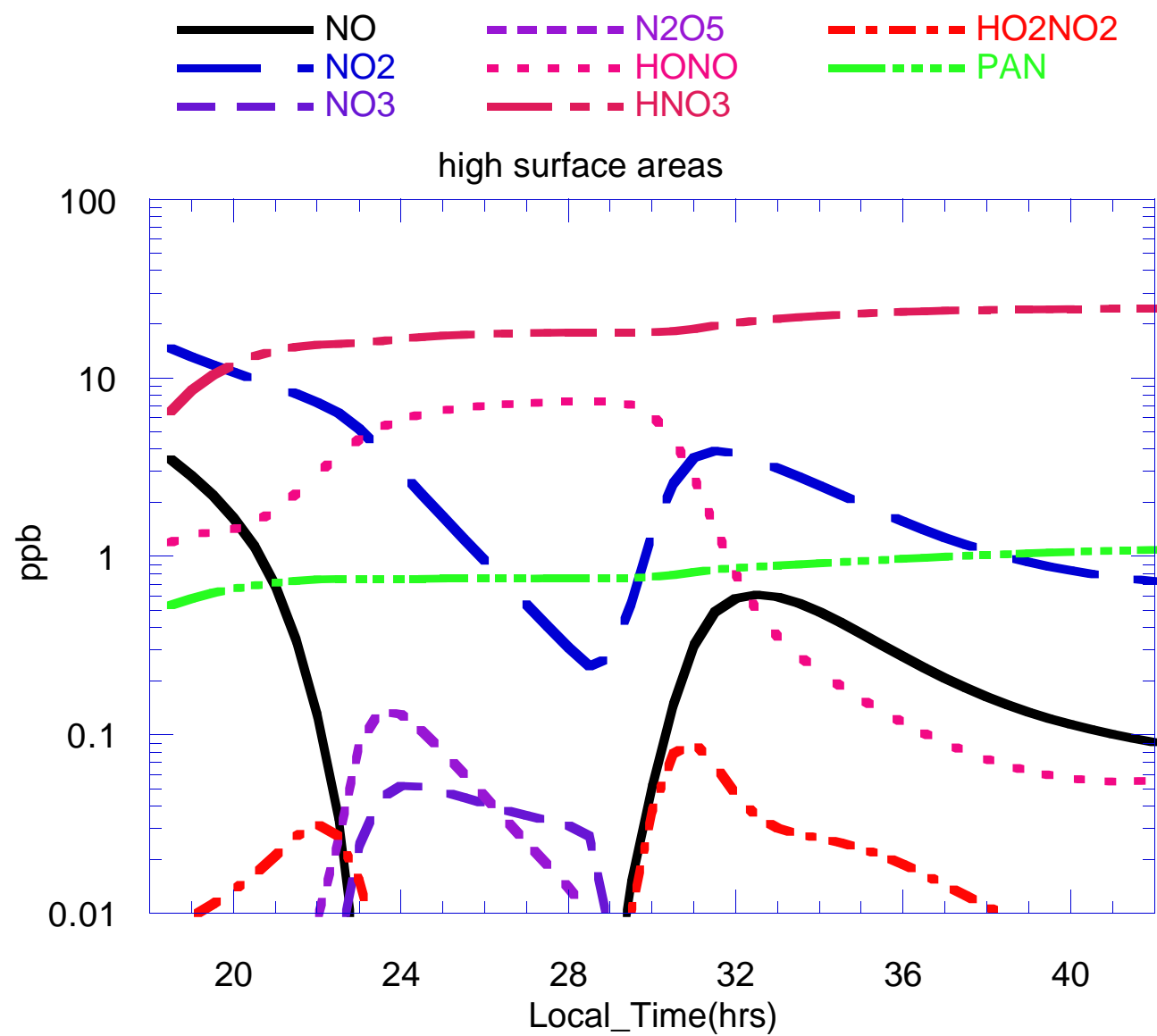- HC chemistry scheme follows simplified RADM mechanism.

Initial Conditions
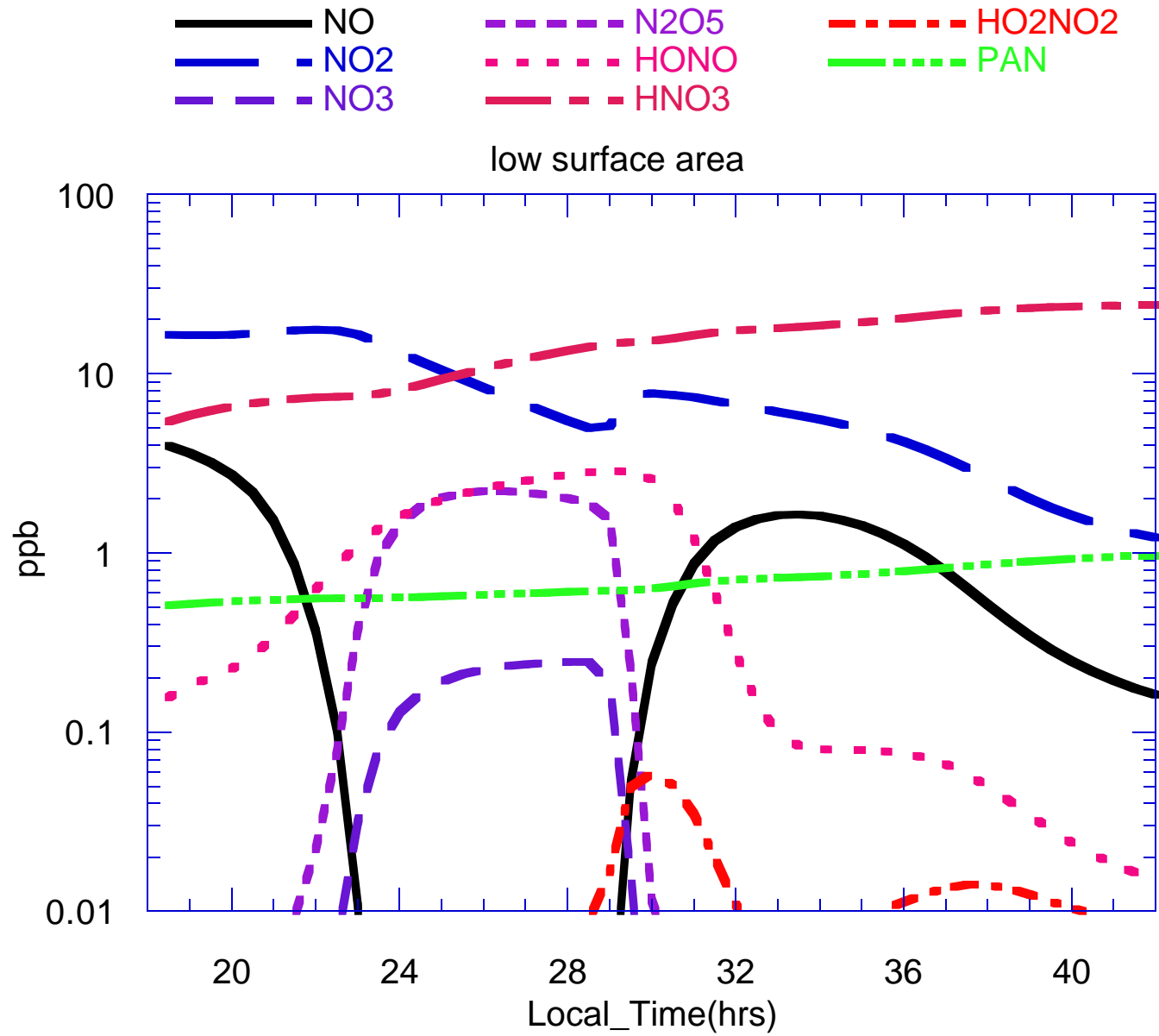
- NOx 25 ppbv (based on mixing ratios measured in plumes by Gaffney et al.)

- NO/NOx ratio is set to 0.3 (inferred from the ADE data)

- Hydrocarbons from the measurements made by Paul Doskey in a plume encountered on May 26.

- Surface area for soot set at 3.E-05 (high) and for N_2O_5 (Ammonium bisulfate type aerosol) at factor of 10 lower than soot for high case.

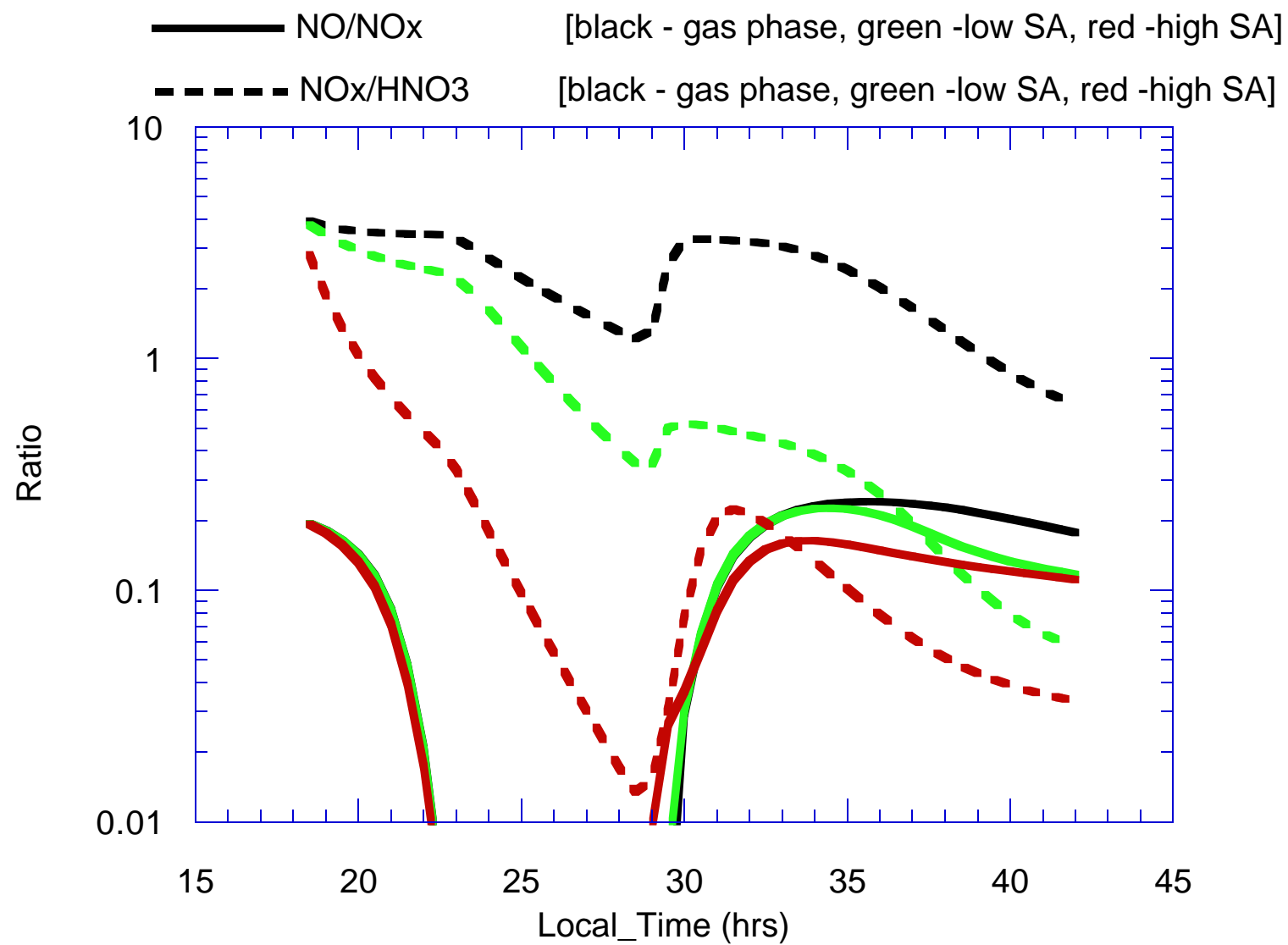- Low SA case is a factor 10 lower.

Caluclated mixing ratios of HONO

gas phase reactions only

Legend: NO, NO2, NO3, N2O5, HONO, HNO3, HO2NO2, PAN

high surface areas

Legend: NO, NO2, NO3, N2O5, HONO, HNO3, HO2NO2, PAN

y-axis: ppb

x-axis: Local_Time(hrs)

low surface area

Legend:
- NO
- NO2
- NO3
- N2O5
- HONO
- HNO3
- HO2NO2
- PAN

Y-axis: ppb

X-axis: Local_Time(hrs)

ozone mixing ratios

Legend:
- gas phase
- High SA -[N2O5 & HONO rxns only]
- Low SA [N2O5 & HONO rxns only]
- Low SA [N2O5, HONO, HNO3 rxns]
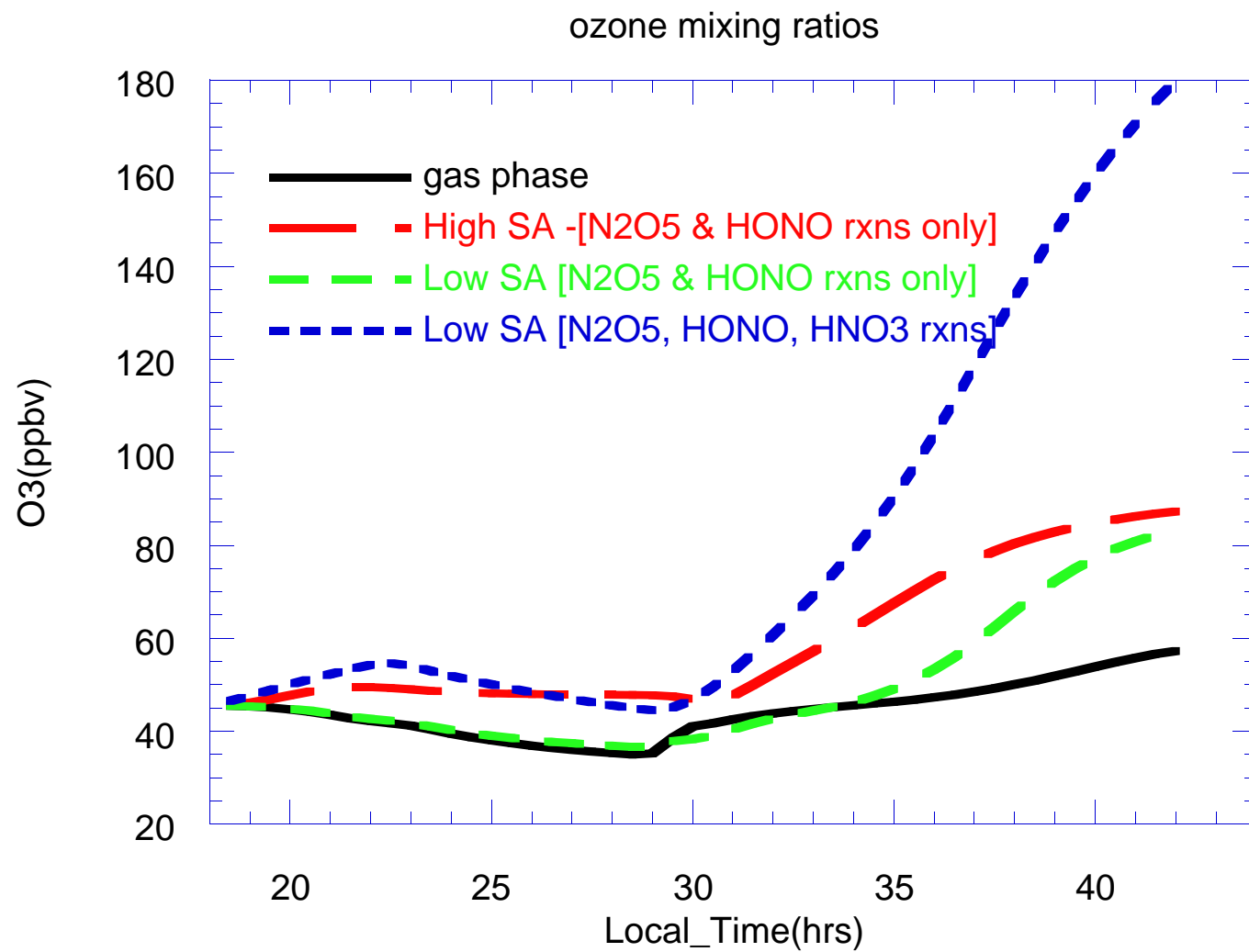
Y-axis: O_3(ppbv)

X-axis: Local_Time(hrs)

Conclusions

- NO_2 conversion to HONO on soot particles would produce ppb levels of HONO during night time

- In the absence of other removal processes (such as dry deposition) a plume containing HONO would lead to additional ozone production of ozone compared to gas phase reactions alone.

- High conversion rates seem unsupportable based on ozone mixing ratios calculated in the plume